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Yokota et al.

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[45] **Aug. 28, 1973**

[54] **TREATMENT PROCESS FOR REMOVAL OF METALS AND TREATING AGENT THEREFOR**

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[21] Appl. No.: **104,160**

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **210/36,** 55/72, 55/73, 55/74, 210/38

[51] **Int. Cl.** **B01d 15/00**

[58] **Field of Search** 55/72, 74, 75; 210/24, 36, 38; 260/429, 429.5

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Primary Examiner—Samih N. Zaharna
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[57] **ABSTRACT**

A treament process for removing metals from a gaseous phase or liquid phase metal-containing material using a solid treating agent consisting of a carrier material and a compound deposited thereon, such compound being selected from (a) an organic compound capable of forming a mercaptide compound of a metal, which compound has the —SH radical or an alkali salt thereof in its molecule and may also have a member or members selected from the group consisting of the —N=, —S—, -NH-, —N=N-and —NH-NH- radicals in the same molecule; (b) an organic compound capable of forming a mercaptide compound of a metal, which compound has the



radical in its molecule and also have a member or members selected from the group consisting of the —N=, —S—, —NH—, —N=N—, and —NH—NH— radicals in the same molecule; and (c) an organic compound capable of forming a chelate compound of a metal, which compound has the —OH radical in its molecule and also a member or members selected from the group consisting of the —N= and $—NH_2$ radicals in the same molecule.

7 Claims, No Drawings

TREATMENT PROCESS FOR REMOVAL OF METALS AND TREATING AGENT THEREFOR

This invention relates to an improved treatment process by which residual metals contained in gaseous phase (a terminology inclusive of vapor phase) or liquid phase (a terminology inclusive of the liquid phase in a slurry state) materials to be treated can be removed with an excellent removal capacity, down to a low concentration such as can be indicated in ppb units (1 ppb = 1/1000 ppm), using a readily manufactured and readily available treating agent, while maintaining the foregoing capacity of the treating agent for a prolonged period of time and, moreover, at an especial advantage from the standpoint of the equipment and operations involved.

More specifically, the invention relates to a treatment process for removing metals and a treating agent to be used therein, such process being characterized in that the gaseous or liquid phase metal-containing material to be treated is contacted with in solid treating agent which consists of a carrier material supporting by adsorption thereto a compound selected from the group consisting of

a. an organic compound capable of forming a mercaptide compound of a metal, which compound has the —SH radical or an alkali salt thereof in the molecule and may also have a member or members selected from the group consisting of —N=, —S—, —NH—, —N=N— and —NH—NH— radicals in the same molecule;

b. an organic compound capable of forming a mercaptide compound of a metal, which compound has the



radical in the molecule and also has a member or members selected from the group consisting of the —N=, —S—, —NH—, —N=N— and —NH—NH— radicals in the same molecule; and

c. an organic compound which can form a chelate compound of a metal, which compound has the —OH radical in the molecule and also has a member or members selected from the group consisting of the —N= and $—NH_2$ radicals in the same molecule.

Heretofore, the following metal-containing waste gases, waste liquids and the like are known: concentrated aqueous caustic alkali solution obtained from the electrolysis of alkali salts by the mercury cell; hydrogen gas and synthetic hydrochloric acid synthesized from said hydrogen gas and chlorine gas; various other waste water and waste gases formed during the electrolysis of alkali salts by the mercury cell; various waste liquids and waste gases which are produced during the smelting of zinc, mercury, copper and other metals; waste water of the plating industry; waste liquors containing catalysts or decomposed products thereof, which have been used in the polymerization reaction and other catalytic reactions; various waste liquors of the synthetic chemical industry which use metal compounds; and other metal-containing and especially heavy metal-containing waste gases, waste liquids and the like, which are produced in a broad range of inorganic and organic industries and the mining industry.

Lately, the desire is especially great that these metals be removed from these generally harmful metal-containing waste gases and waste liquids to such a low

content as to be substantially tolerable for preventing the environmental pollution, inclusive of the instances in which the conjoint purpose is to recover the metals contained.

The usual method which is employed for removing the metals from the metal-containing materials to be treated is either that in which the metal is precipitated or flocculated by adding a precipitating agent or a flocculating agent and thereafter isolating and collecting the metal, or that in which the metal is absorbed and isolated by using an adsorbent such as active carbon.

However, in the case of the former method it was exceedingly difficult to separate the supernatant liquid and the metal-containing precipitate or flocculate from the large quantity of the waste liquid being treated. Further, there was the necessity for the use of a great quantity of the treating agent and the need for a large scale precipitating apparatus or precision filtration apparatus for fully separating and removing the fine metal-containing solids portion. On the other hand, in the case of the latter method, it was very difficult to reduce the concentration of the residual metal in the liquid to as low a content as desired.

Further as the method of removing the metals from the gaseous phase metal-containing materials to be treated, and particularly the removal of the vapor phase metals, inter alia mercury contained in the gas, the method known heretofore was either that of cooling the gas to a low temperature at normal pressure or superatmospheric pressure of 3–5 kg/cm² and condensing the mercury vapor and separating same, or that in which the mercury was absorbed by passing the gas through a layer packed with active carbon or a molecular sieve.

However, the former of these methods requires a large-scale cooling equipment for cooling the gas, while the latter method has the drawback that in the case of active carbon and molecular sieve the amount of mercury absorbed in the gas is small, with the consequence that they are relatively poor in efficiency as adsorbents for they are required to be used in large quantities.

Again, as a chemical method of removing metals from metal-containing materials in the gaseous phase, there is a method of removing mercury from hydrogen gas as a mercuric chloride by treating with a hypochlorite. Further, a method of treatment by means of a sulfuric acid-added potassium permanganate solution is also practiced, but there is the drawback that the adjustment during the operation is difficult and that recontamination of the gas by means of the excess chlorine takes place.

In addition, as a method of treatment with ozone, there is a method in which the gas containing the mercury is treated with ozone and separation is carried out with an electrostatic separator or mechanical filtration, but difficulty is involved in the separation or filtration operation.

While several instances of possible methods have been described hereinbefore, the removal of metals from the gaseous or liquid phase metal-containing materials being treated, inclusive of the instances where the conjoint purpose is to recover the metals, not only involves considerable difficulties but also possesses drawbacks which need solution. There is particularly the limitation that a costly method from the standpoint of the treating agent, apparatus and operations cannot be utilized for the solution of the foregoing difficulties

and drawbacks, since in the case of these waste liquids and waste gases the amount to be treated is usually very great, and hence the solution of the problem is made very great, and hence the solution of the problem is made much more difficult. This is the present state of affairs.

As a result of our researches with a view to overcoming the foregoing difficulties and drawbacks and providing a method which can be carried out advantageously without being subjected to the aforesaid limitation, we found that by using a solid treating agent to which has been adsorbed and deposited a certain organic compound which is capable of forming a mercaptide compound or an N,O- co-ordinate chelate compound of a heavy metal, metals could be removed with a remarkably excellent metal capturing capacity from the metal-containing material being treated regardless of whether it is in a gaseous or liquid phase and moreover with this removal capacity being maintained stably over a prolonged period of time. On the basis of this finding, we were able to succeed in developing a treatment method which demonstrates greatly improved results.

Further, it was found that the coordinative conditions involving (1) the use as the adsorptive carrier material a carbonaceous material or other adsorptive carrier materials, which have been used heretofore independently for these treatments, and (2) the deposition thereon by adsorption thereto of the hereinbefore described organic compound were indispensable for achieving the objectives of the invention, and that a metal captivating and removal capacity of high degree wholly unexpected by the use of the organic compound and carrier separately was demonstrated.

It is therefore an object of the present invention to provide an improved treatment process by which metals contained in a gaseous or liquid phase metal-containing material being treated can be captured and removed with remarkably excellent removal capacity, using a readily manufactured and readily available inexpensive treating agent. Another object is to provide a method of removing the aforesaid metals advantageously with an exceedingly simple apparatus and operation with no limitation from the cost standpoint while maintaining the metal removal capacity of the aforesaid treating agent over a prolonged period of time. A further object is to provide an inexpensive treating agent of high performance, which is suitable for use in the hereinbefore described treatment.

Other objects and advantages of the present invention will become apparent from the following description.

In the process of the invention a solid treating agent consisting of an organic compound capable of forming a mercaptide compound or an N,O- co-ordinate chelate compound of a metal, which is supported by a carrier material by adsorption thereto is used.

The foregoing organic compound is selected from the following groups (a), (b) and (c);

a. an organic compound capable of forming a mercaptide compound of a metal, which compound has the —SH radical or an alkali salt thereof in the molecule and may also have a member selected from the group consisting of the —N=, —S—, —NH—, —N=N— and —NH—NH— radicals in the same molecule;

b. an organic compound capable of forming a mercaptide compound of a metal, which compound has the



radical in the molecule and also has a member selected from the group consisting of the —N=, —S—, —NH—, —N=H— and —NH—NH— radicals in the same molecule; and

c. an organic compound capable of forming an N,O coordinate chelate compound of a metal, which compound has the —OH radical in the molecule and also has a member selected from the group consisting of the 13 N= and $-NH_2$ radicals in the same molecule.

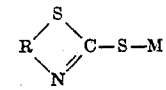
As examples of the these compounds, those of group (a), above include the following groups (1) – (4) :

1. Mercaptide compounds of the formula

R-S-M

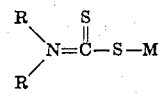
wherein R is an aromatic group or a group having a terminal —CH= or $-CH_2-$ radical, and M is hydrogen or an alkali metal.

2. Thiazole compounds of the formula



wherein R is an aromatic group and M is hydrogen or an alkali metal.

3. Di-alkyldithiocarbamic acid of the formula



wherein R is a $C_1 - C_{10}$ alkyl radical, methyl, ethyl, n-butyl, etc., and M is hydrogen or an alkali metal. (4) Xanthates of the formula

R—O—C—S—M

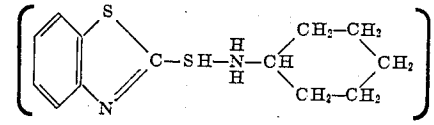
wherein R is butyl or isopropyl and M is hydrogen or an alkali metal.

Specific examples of the compounds or group (a) include the following organic compounds which can form a mercaptide compound of a metal.

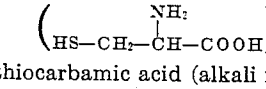
2-Aminoethanethiol ($H_2NCH_2CH_2SH$)

butyl-mercaptan (C_4H_9SH)

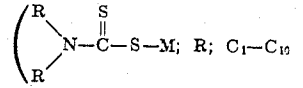
Cyclohexylamine salt of 2-mercaptobenzothiazole



◊ L-cysteine

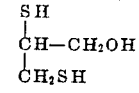


◊ Di-alkyldithiocarbamic acid (alkali metal salt)

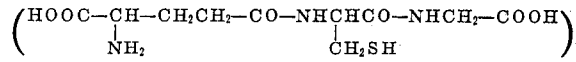


alkyl radical like as methyl, ethyl and n-butyl, M; alkali metal)

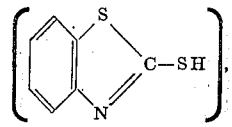
◊ 2.3-dimercapto-1-propanol



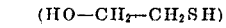
◊ Glutathione



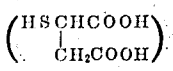
◊ 2-mercaptobenzothiazole



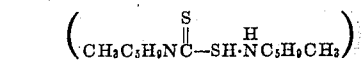
◊ and its alkali metal salts.
◊ 2-mercaptoethanol



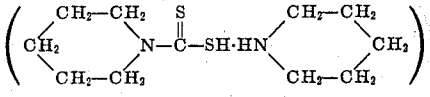
◊ dl-mercaptosuccinic acid



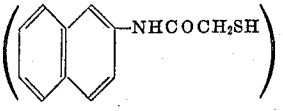
◊ Pipecolin pipecolyl dithio carbamate



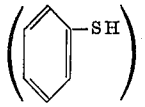
◊ Piperidine pentamethylene dithio carbamate



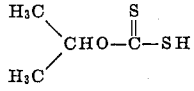
◊ Thioacetic acid (CH_3COSH)
◊ Thioglycolic acid ($HS{\cdot}CH_2COOH$) o and its alkali metal salts.
◊ Thionalide



◊ Thiophenol



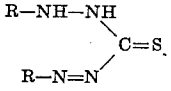
◊ and its alkali metal salts.
◊ Isopropyl xanthic acid



◊ and its alkali metal salts.

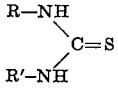
Examples of the compounds of group (b), above, include the following :

1. Thiocarbazones of the formula



wherein R is an aromatic group.

2. Thioureas of the formula



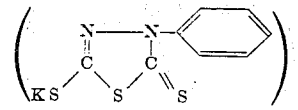
wherein R and R′ are each an aromatic group or a C_1 – C_{10} alkyl radical.

3. 2-Mercaptobenzimidazole.

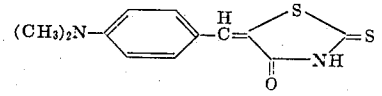
4. 2-Mercaptoimidazoline.

Specific examples of the compounds of group (b) include the following organic compounds which can form a mercaptide compound of a metal.

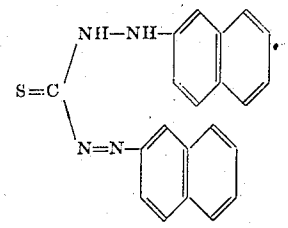
◊ Bismuthiol II



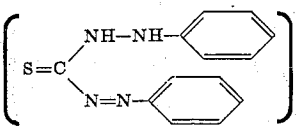
◊ p-dimethylaminobenzylidenerhodamine



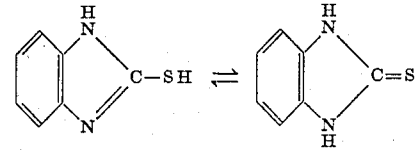
◊ Di-β-naphthylthiocarbazone



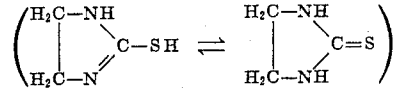
◊ Dithizone



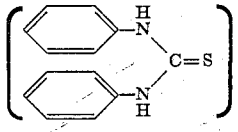
◊ 2-mercaptobenzimidazole (O-phenylene thiourea)



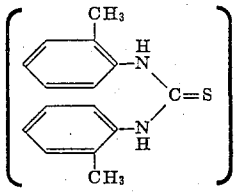
◊ 2-mercaptoimidazoline (ethylenethiourea)



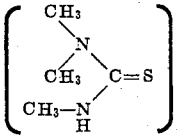
◊ Thiocarbanilide



◊ Di-orthotolylthiourea

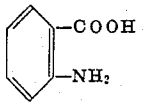


◊ Trimethylthiourea

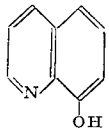


On the other hand, specific examples of the compounds of group (c) include the following organic compounds which can form an N,O— co-ordinate chelate compound of a metal,

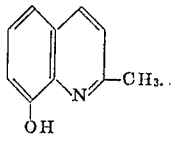
Anthranylic acid



Oxine



2-methyl oxine, i.e., 8 hydroxyquinaldine



While the hereinabove illustrated organic compounds, which are useable in the present invention, include both those which are water-soluble as well as water-insoluble, these compounds can be dissolved in such solvents which are suitable for the several compounds and be deposited on a carrier material by adsorption thereto.

As these solvents, mention can be made of such, for example, as water, aqueous alkaline solutions containing an inorganic alkaline substance such as alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates and ammonia; methanol, ethanol, propanol, butanol and other $C_1 - C_{10}$ aliphatic alcohols; the halogenated lower hydrocarbons such as dichloromethane, trichloromethane and trichloroethylene; dilower alkyl carbonyls such as dimethyl carbonyl; carbon tetrachloride; chloroform; and acetone.

These solvents are imposed no restrictions and can be used so long as they do not react with the foregoing organic compounds (i.e. are inert thereto) and can dissolve same. Of these solvents, preferred are those which can be readily removed after the aforesaid organic compounds have been deposited on the carrier material by adsorption thereto by such means as water-washing, washing in a dilute aqueous acid solution, evaporation, vacuum drying and air drying.

Needless to say, the use of a solvent can be dispensed with in the case where the organic compound used is one which is normally liquid.

In effecting the deposition on the carrier material by adsorption thereto of the hereinbefore described organic compound or a solvent solution thereof, any method by which the organic compound or solution thereof is brought fully into contact with the carrier material can be employed. For example, the carrier material can be submitted to an immersion treatment in these solutions, or the solutions can be flowed down through a column packed with the carrier material, or various other methods of contacting the liquid phase with the solid phase can be utilized. This operation of effecting the deposition of the organic compound on the carrier material by adsorption of the former to the latter is usually carried out at room temperature but, if desired, the operation can be carried out under heated conditions of 30° – 70°C.

After the deposition treatment, the resulting solid treating agent can be directly used but, if desired, it may be used after having been submitted to water-washing, washing in a dilute aqueous acid solution, evaporation, vacuum drying, air drying and other treatments to remove the solvent contained therein.

As the carrier material constituting the substrate of the solid treating agent to be used in the present invention, those obtained from natural or artificial sources can be widely used, but those selected from the group consisting of the carbon carriers such as active carbon and bone black, silica gel, zeolite and silica-alumina gel containing at least 50 percent by weight of silica gel demonstrate exceedingly superb improved results and thus are recommended. If desired, the organic high molecular weight adsorbents and molecular sieves can be used as the carrier material, but these are not desirable because of their high cost. Further, such carriers as alumina, magnesia and the naturally obtained quartz sand can also be used, but results obtained are inferior to those obtained in the case of the use of the hereinabove recommended carrier materials.

The size of the carrier particles can be varied over a broad range and those on the order of 80 180 mesh, and preferably 6 – 2 – mesh, may usually be used. Again, the amount in which the aforesaid organic compound is deposited on the carrier material by adsorption thereto can also be varied over a broad range, and an amount on the order of 1 – 30 percent by weight, and preferably 2 – 20 percent by weight, based on the carrier material, may usually be used. The particles size of the carrier material and the amount of the organic compound to be deposited thereon by adsorption thereto, as indicated above, can be suitably modified in accordance with the class of the carrier material, the class of the organic compound, the class of the material to be treated, the method used in effecting the contact of the material to be treated and the solid treating agent and the treatment speed.

No special restriction is imposed as to the method to be used in effecting the contact between the solid treating agent, such as hereinabove described, and the gaseous or liquid phase metal-containing material to be treated in accordance with the invention process. All of the liquid-solid phase or gaseous-solid phase contacting methods which are capable of fully contacting the treating agent with the material being treated can be utilized. While the batch method of contact can be employed, preferred is a continuous contact method such, for example, as the column method.

For example, the material being treated can be caused to flow downwardly through a column packed with the solid treating agent or conversely be caused to flow upwardly through the column; or while forming a fluidized bed of the solid treating agent the gaseous phase material being treated can be passed through such bed; or if the material being treated is of liquid phase, it can be sprayed. While the contact treatment can be carried out in a single stage, it also can be carried out in a multistage fashion by providing a plurality of contact zones through which the material being treated is passed. While there is no particular restriction imposed as to the temperature at which the treating agent and the material being treated are contacted, a range of 5° – 35°C. is frequently employed.

The contact time or speed of the solid treating agent with the gaseous or liquid phase material being treated can be readily varied by those skilled in the art in accordance with the class of the organic compound, the class and particle size of the carrier material and amount of the organic compound supported, the class of the material being treated and the method of contacting the solid treating agent with the material being treated. In general, the optimum conditions can be readily determined experimentally over a range of SV (space velocity) = 0.2 – 20 1/hr in the case the material being treated is of liquid phase and over a broad range on the order of SV = 100 – 5000 1/hr in the case the

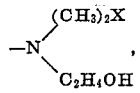
material being treated is of gaseous phase, in accordance with the hereinbefore indicated various factors.

As the metals to be contained in the gaseous or liquid phase metal-containing material to be treated by the invention process, those metals selected from the group consisting of Hg, Au, Bi, Cd, Co, Cr, Cu, Ni, Pb, Zn, Ag, Mn, Fe, Mo, Ti, Mg and Al can be mentioned. The invention process can be employed with special advantage in the treatment of a gaseous or liquid phase material containing at least one of the foregoing metals.

The hereinbefore described organic compound is preferably chosen in accordance with the class of the metal contained in the material to be treated. For example, thionalide, 2-mercaptobenzothiazole and p-dimethylaminobenzilidene-rhodanine are preferably used in the case of Hg, Cu, Au, Ag, Cd and Pb; oxine and 2-mercaptobenzothiazole, in the case of Bi, Co, Ni and Zn; and oxine and 8-hydroxyquinaldine, in the case of Mn, Cr, Fe, Mo, Ti and Mg. When the material to be treated is one containing a plurality of metals, a plurality of organic compounds can be used.

In the case where the material to be treated is one of liquid phase, it is possible according to the invention process to pretreat the material with an anion exchange resin and thereafter contact the so pretreated metal-containing material with the aforesaid solid treating agent. In general, when the content of metal is very great and the recovery of the metal is also intended, a pretreatment of this kind is desirable. Since the recovery of the metal from the anion exchange resin is a relatively simple matter, the metal contained in the metal-containing material being treated can be recovered with this pretreatment, after which the reduced amount of metal contained in the residual liquid can be contacted with the solid treating agent to effect its removal by fixation to the treating agent.

As such an anion exchange resin, mention can be made of those having as the exchange group such, for example, as $-N-(CH_3)_3X$,



$-N(R)_2$, $-NH(R)$, $-NH_2$ and $-N(CH_3)_2$, wherein X is an anion such as Cl^-, OH^-, etc., and R is an alkyl radical such as CH_3, C_2H_5, etc.

The pretreatment operation is carried out in the following manner. The material being treated is passed successively through a column packed with the hereinbefore described anion exchange resin. Alternatively, the anion exchange resin is introduced into the treatment tank and the adsorption is carried out with stirring, after which the resin is separated from the treated liquid.

The invention process can be applied as a treatment method for removing metals from the gaseous or liquid phase metal-containing materials extending over a wide range from those which are acid to those which are alkaline. For example, the invention process can be applied to the removal of Hg from the concentrated aqueous caustic alkali solutions obtained in the mercury cell method of electrolysis of alkali salts; the removal of Hg of the hydrogen gas evolved during the aforesaid electrolysis; the removal of Hg contained in the synthetic hydrochloric acid synthesized from hydrogen gas and chlorine gas; in addition, the removal of Hg from the various waste gases and water that are produced during the mercury method of electrolysis of alkali salts; the removal of Hg, Cd, Mn, Cr, Cu, Fe, etc., from the various waste gases and water which are produced during the smelting of various metals; the removal of Cr and Cu from the waste water of the plating industry; the removal of Hg, Cd, Mn, Cr, Cu, Fe, etc., from the waste liquids containing catalysts or decomposition products thereof, as well as from the waste gases and water produced in the synthetic chemical industry; and the removal of metals contained in a wide range of other gaseous and liquid phase materials.

The following examples and control experiments are given to illustrate several modes of practicing the present invention.

EXAMPLES 1 - 2 AND CONTROL 1

Three hundred ml of carbon tetrachloride in which were dissolved 150 mg of dithizone were flowed down through a glass tube of 8 mm inside diameter packed with 5 grams of active carbon thereby causing the adsorption to and deposition on the active carbon layer of dithizone. The amount of dithizone absorbed and deposited was about 150 mg. This dithizone-supporting carrier was left standing for 24 hours to cause the carbon tetrachloride to volatilize. This was followed by flowing a saline prepared from mercuric chloride and sodium chloride (mercury content 1.4 mg per liter) down through the tube at the rate of 130 cc per hour. This test was repeated ten times. In every case the mercury concentration of the effluent became less than 5 ppb.

Further, about 5 grams of the dithizone-supporting carrier prepared as in Example 1 were added to 200 ml of saline containing 1.4 mg/l of mercury, the contact being carried out for one hour with gentle stirring (Example 2), with the result that the mercury concentration of the aqueous solution became less than 5 ppb.

A control, the experiment was carried out exactly as in Example 1 except that the adsorption to and deposition on the active carbon of the dithizone was not carried out and 5 grams of active carbon were used (Control 1). The test was repeated 10 times and in every instance the mercury concentration of the effluent was above 420 ppb.

The results obtained in the foregoing experiments are shown in Table 1.

TABLE 1

	Treating agent					Metal concentration (p.p.b.)	
	Organic compound		Carrier				
Experiment No.	Name	Amount adsorbed (wt. percent)	Name	Weight (g.)	Metal to be removed	Before treatment	After treatment
Example 1	Dithizone	3	Active carbon	5	Hg	1,400	<5
Example 2 (batch method)	do	3	do	5	Hg	1,400	<5
Control 1			do	5	Hg	1,400	>420

As is apparent from the results given in the Table 1, above, it can be seen that totally unexpected results were achieved in accordance with the invention process as compared with the case where the adsorbent carrier was used alone.

EXAMPLE 3 AND CONTROL 2

The experiments were carried out as in Example 1 and Control 1 except that 2-mercaptobenzothiazole and silica gel were used as the organic compound and carrier, respectively, and the carrier weight, amount of the organic compound deposited thereon by adsorption and the Hg concentration of the material treated were varied. The results obtained are shown in Table 2.

TABLE 2

Experiment No.	Organic compound: Name	Organic compound: Amount deposited (wt. percent)	Carrier: Name	Carrier: Weight (g.)	Metal to be removed	Metal concentration (p.p.b.): Before treatment	Metal concentration (p.p.b.): After treatment
Example 3	2-mercaptobenzothiazole	5	Silica gel	10	Hg	13,900	<5
Control 2			do	10	Hg	13,900	>13,000

The results presented in Table 2 show, as in Table 1, the totally unexpected results that can be obtained by the invention process.

EXAMPLE 4

One hundred mg of thionalide in solution in 100 ml of dichloroethane were flow down through a glass tube of 8 mm inside diameter packed with 5 grams of active carbon thereby effecting the thorough adsorption to and deposition on the active carbon layer of the thionalide, followed by removal of the solvent by blowing in air. A solution containing 5.6 mg per liter of mercury was flowed down through this thionalidesupporting carrier at the rate of 130 ml per hour, whereupon the mercury concentration of the effluent became less than 50 ppb.

EXAMPLES 5 – 28

The experiments were carried as in Example 4, using as the method of contact either the column method or the batch method described in Example 2 and various combinations of the organic compound and carrier, with the metals to be removed of various classes. The results obtained are shown in Table 3.

TABLE 3

Experiment No.	Solid treating agent: Organic compound used: Name	Amount deposited (wt. percent)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example 5	2-mercaptobenzothiazole	10	CH_2Cl_2	Active carbon	5
Example 6	Thionalide	2	$CHCl_3$	do	5
Example 7	2-mercaptobenzothiazole	10	CH_2Cl_2	do	5
Example 8	Oxine plus 2-methyloxine	2	$(CH_3)_2CO$	do	5
Example 9	p-Dimethylaminobenzylidene rhodanine	2	$(CH_3)_2CO$	do	5
Example 10	Thionalide	2	$CHCl_3$	do	5
Example 11	2-methyloxine plus 2-mercaptobenzothiazole	12	CH_2Cl_2	do	5
Example 12	Dithizone	2	0.5% aq. ammonia sol	do	5
Example 13	2-mercaptobenzothiazole	20	3% aq. NaOH sol	do	5,000
Example 14	2-mercaptobenzothiazole	10	Acetone	do	5,000
Example 15	2-mercaptobenzothiazole (Na salt)	8	Water	do	30
Example 16	Bismuthol II	7.5	do	Bone black	40
Example 17	Na salt of diethyldithiocarbamic acid	5	do	Active carbon	40
Example 18	Na salt of isopropyl xanthic acid	4.5	do	do	30
Example 19	Pipecoline pipecolyc dithiocarbamate	3.5	3% aq. NaOH sol	do	40
Example 20	2,3-dimercapto-1-propanol	3.0	Water	do	40
Example 21	2-mercaptoethanol	2.8	do	do	30
Example 22	Na salt of 2-mercaptobenzothiazole	2.3	do	Silica gel	100
Example 23	Thionalide	3.0	$CHCl_3$	Active carbon	5
Example 24	Bismuthiol II	7.5	Water	do	5
Example 25	2-mercaptobenzothiazole plus anthranilic acid	Total 10	3% aq. NaOH sol	do	5
Example 26	p-Dimethylaminobenzylidene rhodanine plus 2-mercaptobenzothiazole.	Total 15	Acetone	do	5
Example 27	Oxine plus pipecoline pipecolyl dithiocarbamate	do	do	do	5
Example 28	8-hydroxy quinaldine plus p-dimethylamino-benzylidene rhodanine.	5	do	do	5

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method), l./hr.	Material treated: Metal to be removed	Material treated: Property	Metal concentration (p.p.b.): Before treatment	Metal concentration (p.p.b.): After treatment
Example 5	6.5	Hg	Aq. sol	5,600	5
Example 6	10	Hg	Aq. sol	5,600	50
		Cu	Same as above	2,500	10
Example 7		Hg	Aq. sol	5,600	5
		Fe	Same as above	300	
Example 8	7.5	Cr	Aq. sol	500	70
		Mn	Same as above	700	50
Example 9	7.0	Hg	Aq. sol	13,900	5
Example 10	7.8	Cd	Same as above	200	30
Example 11	8.0	Hg	do	5,600	5
Example 12	9.0	Hg	do	9,800	5
Example 13	10.5	Hg	do	10,200	5
Example 14	Contact time 1 hour	Hg	Aq. slurry	25,000	250
Example 15	Contact time 2.5 hours	Hg	Aq. sol	8,200	7
		Cd	Same as above	600	40
Example 16	do	Hg	Aq. sol	5,500	9
		Cu	Same as above	500	50
Example 17	2.1	Hg	Aq. sol	5,600	8
		Cu	Same as above	1,200	54

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method), l./hr.	Material treated: Metal to be removed	Material treated: Property	Metal concentration (p.p.b.): Before treatment	Metal concentration (p.p.b.): After treatment
Example 18	2.1	Hg	Aq. sol	8,200	6
Example 19	1.1	Hg	Same as above	7,800	8
Example 20	1.0	Hg	do	2,500	10
Example 21	1.0	Hg	do	2,700	12
Example 22	2.0	Hg	Aq. sol	8,200	8
		Cd	Same as above	600	50
Example 23	10	Hg	Aq. sol	9,800	50
		Ag	Same as above	1,200	70
		Pb	do	4,100	75
Example 24	8.0	Al	Aq. sol	1,600	100
		Cd	Same as above	750	40
		Cu	do	1,200	55
		Hg	do	9,800	20
Example 25	7.0	Co	Aq. sol	900	50
		Zn	Same as above	1,500	55
		Cd	do	3,500	25
		Ni	do	700	40
		Hg	do	7,700	7
Example 26	7.5	Ag	Aq. sol	2,400	35
		Bi	Same as above	420	15
Example 27	6.0	Mn	Aq. sol	1,200	60
		Cr	Same as above	720	75
		Fe	do	2,900	25
Example 28	6.5	Mo	Aq. sol	950	60
		Ti	Same as above	1,300	75
		Mg	do	750	80
		Ag	do	1,200	30

EXAMPLES 29 - 55 AND CONTROL 3

Experiments were carried out with the mercury-containing materials to be treated being those having an acid property and those having an alkaline property. As the former, mercury-containing concentrated aqueous hydrochloric acid solutions were used while, as the latter, mercury-containing aqueous caustic alkali solutions were used. The results obtained are shown in Table 4. Also shown in Table 4 are the results obtained as Control 3 wherein the experiment was carried out exactly as in Example 53 except that an organic compound was not deposited on the active carbon.

TABLE 4

Experiment No.	Solid treating agent: Organic compound used: Name	Amount deposited (wt. percent)	Solvent used	Carrier: Name	Carrier: Weight (g.)
Example 29	Na salt of 2-mercaptobenzothiazole	10	Water	Active carbon	100
Example 30	2-mercaptobenzothiazole	About 20	3% aq. NaOH sol	do	40
Example 31	Pipecoline pipecolyl dithiocarbamate	About 10	Acetone	do	20
Example 32	Thionalide	About 2.5	Dichloromethane	do	20
Example 33	Dithizone	About 1.0	CCl_4	do	10
Example 34	p-Dimethylaminobenzylidene rhodanine	About 4.0	Acetone	do	10
Example 35	Di-β-naphthyl thiocarbazone	About 1.0	Chloroform	do	10
Example 36	2-mercaptobenzothiazole	About 2.0	3% aq. NaOH sol	Bone black	10
Example 37	Bismuthiol II	About 3.0	Water	Active carbon	20
Example 38	Thiophenol	About 1.0	Ethanol	do	10
Example 39	Piperidine pentamethylene thiocarbamate	About 5.0	Acetone	do	10
Example 40	2-mercaptoimidazoline	About 2.0	Methanol	do	10
Example 41	Sodium diethyldithiocarbamate	About 5.0	Water	do	20
Example 42	2-mercaptobenzothiazole	About 3.0	Acetone	Silica gel	10
Example 43	p-Dimethylaminobenzylidene rhodanine	About 1.5	do	Zeolite	20
Example 44	Sodium diethyldithiocarbamate	About 5.0	6% aq. NaOH sol	Active carbon	150
Example 45	2-mercaptobenzothiazole	10	Acetone	do	40
Example 46	L-cysteine	6.0	Water	Pwd. active carbon	50
Example 47	Sodium salt of 2-mercaptobenzothiazole	About 5.0	do	Active carbon	40
Example 48	Glutathione (reduced type)	About 3.0	do	Pwd. active carbon	50
Example 49	L-cysteine	About 2.0	Weak alkali	Molecular sieve	40
Example 50	Bismuthiol II	1.5	Water	Active carbon	40
Example 51	Sodium salt of thiophenol	1.0	Weak alkali	Pwd. active carbon	50
Example 52	2-mercaptobenzothiazole	About 1.5	Acetone	Zeolite	40
Example 53	Thioglycolic acid	About 1.0	Water	Active carbon	40
Example 54	Di-β-naphthylcarbazone	About 2.0	Chloroform	do	40
Example 55	Thionalide	About 2.5	Dichloromethane	Pwd. active carbon	50
Control 3				Active carbon	40

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method), l./hr.	Material treated: Metal to be removed	Material treated: Property	Metal concentration (p.p.b.): Before treatment	Metal concentration (p.p.b.): 120 hrs. later
Example 29	Contact time 2 hours	Hg	Conc. HCl	2,500	7
Example 30	11.0	Hg	Conc. HCl	1,700	4
Example 31	Contact time 2 hours	Hg	Conc. HCl	1,700	6
Example 32	Contact time 2.5 hours	Hg	Conc. HCl	1,700	30
Example 33	do	Hg	Conc. HCl	1,700	28
Example 34	Contact time 2.0 hours	Hg	Conc. HCl	1,700	5
Example 35	Contact time 2.5 hours	Hg	Conc. HCl	1,700	30
Example 36	Contact time 2.0 hours	Hg	Conc. HCl	1,300	12
Example 37	Contact time 3.0 hours	Hg	HCl 35%	1,300	24

Experiment No.	Solid treating agent: Organic compound used: Name	Amount deposited (wt. percent)	Solvent used	Carrier: Name	Weight (g.)
Example 38	Contact time 2.0 hours		Hg	HCl 35%	1,300	30
Example 39	Contact time 2.5 hours		Hg	HCl 35%	1,300	15
Example 40	do		Hg	HCl 35%	1,300	25
Example 41	do		Hg	HCl 35%	1,700	30
Example 42	do		Hg	HCl 35%	1,700	10
Example 43	do		Hg	HCl 35%	1,300	8
Example 44	Contact time 3 hours		Hg	NaOH 25%	150	30
Example 45	0.7		Hg	NaOH 48%	250	15
Example 46	1.5		Hg	KOH 48%	120	10
Example 47	2.0		Hg	NaOH 48%	120	10
Example 48	0.8		Hg	NaOH 48%	200	30
Example 49	1.2		Hg	NaOH 48%	100	15
Example 50	0.5		Hg	NaOH 48%	100	15
Example 51	0.4		Hg	NaOH 48%	130	30
Example 52	0.5		Hg	KOH 45%	200	27
Example 53	0.4		Hg	NaOH 48%	150	25
Example 54	1.2		Hg	KOH 45%	100	30
Example 55	1.5		Hg	NaOH 48%	130	30
Control 3	0.4		Hg		150	120

EXAMPLES 56 – 67 AND CONTROL 4

Sixty grams of 2-mercaptobenzothiazole were dissolved in 1.2 liters of a caustic soda solution of 3% concentration, after which the resulting solution was flowed down through 300 grams of active carbon of 6 – 20 mesh to effect the full adsorption of the former to the latter. The amount adsorbed was about 18 percent by weight based on the active carbon.

After water-washing and air drying the 2-mercaptobenzothiazole-adsorbed active carbon particles, they were packed in an acrylic resin tube of 60 mm inside diameter and about 25 cm high. This was followed by passing hydrogen gas containing 9.1 mg per cubic meter of mercury through the tube at a space velocity of 2500 l/hr at room temperature, whereupon the mercury content of the hydrogen gas after passage through the tube was 0.001 mg/m³ 6 hours later, 0.002 mg/cm³ 30 hours later and 0.002 mg/m³ 90 hours later.

Experiments were carried out as in the hereinabove described Example 56, varying the organic compound and the class of the carrier. The results obtained are shown in Table 5, below, along with the results of Example 56. Also presented are the results of Control 4, which was also carried out as in Example 56 but without deposition of an organic compound on the carrier.

TABLE 5

Experiment No.	Solid treating agent: Organic compound used: Name	Amount deposited (wt. percent)	Solvent used	Carrier: Name	Weight (g.)
Example 56	2-mercaptobenzothiazole	18	3% aq. NaOH sol	Active carbon	300
Control 4				do	300
Example 57	p-Dimethylaminobenzylidene rhodanine	About 4.0	Acetone	do	25
Example 58	Dithizone	2.0	5% aq. NaOH sol	do	20
Example 59	Thionalide	3.0	Dichloroethane	do	25
Example 60	2-mercaptobenzothiazole	2.0	5% aq. NaOH sol	Bone black	40
Example 61	do	1.0	Same as above	Silica gel	75
Example 62	do	5.0	do	Active carbon	20
Example 63	Pipecoline pipecolyl dithiocarbamate	3.0	Acetone	Zeolite	30
Example 64	2-mercaptobenzothiazole plus pipecoline pipecolyl dithiocarbamate.	6.0	do	Active carbon	25
Example 65	2-mercaptobenzothiazole	10.0	3% aq. NaOH sol	do	25
Example 66	Thiophenol	1.0	Ethanol	do	25
Example 67	Sodium salt of 2-mercaptobenzothiazole	5.0	Water	do	40

Experiment No.	Material treated: Space velocity (l./hr.)	Metal to be removed	Property	Metal concentration (μg./m.³): Before treatment	After treatment: 6 hrs. later	After treatment: 90 hrs. later
Example 56	2,500	Hg	H_2	9,100	1	2
Control 4	2,500	Hg	H_2	9,100	2,700	9,100
Example 57	1,100	Hg	H_2	14,100	2	4
Example 58	4,300	Hg	H_2	9,000	2	7
Example 59	1,800	Hg	H_2	10,600	1	3
Example 60	1,700	Hg	H_2	11,500	2	8
Example 61	1,100	Hg	H_2	8,400	2	10
Example 62	2,000	Hg	Air	1,500	2	7
Example 63	1,400	Hg	H_2	8,200	3	9
Example 64	2,100	Hg	H_2	11,100	3	9
Example 65	850	Hg	HCl	2,100	1	2
Example 66	1,000	Hg	H_2	8,600	4	12
Example 67	2,100	Hg	H_2	9,200	3	7

EXAMPLE 68

An acrylic resin tube of 80 mm inside diameter was packed with 3 grams of an anion exchange resin. The height of the layer was about 1000 mm. When waste water containing 13,700 ppb of mercury was flowed down through this tube at a space velocity of 12 1/hr, the mercury concentration 20 hours later was 150 ppb and 120 hours later was 560 ppb.

Further when this treated liquid was flowed down through an acrylic resin tube of 120 mm inside diameter, which had been packed in advance with a fixed layer (layer height of 1050 mm) of a treating agent consisting of 8.2 kg of 10 – 30 mesh bone black on which had been deposited by adsorption thereto 0.7 kg of 2-mercaptobenzothiazole, the mercury concentration 20 hours later was 2 ppb and 120 hours later was 5 ppb.

EXAMPLE 69

A polyvinyl chloride column having an inside diameter of 280 mm was packed with 52 kg of an anion exchange resin. The layer height was about 1200 mm. When waste water containing 9400 ppb of mercury was flowed down through this column at a space velocity of 10 1/hr, the mercury concentration 25 hours later was 120 ppb and 170 hours later was 860 ppb. Further, when this treated liquid was flowed down through a polyvinyl chloride column having an inside diameter of 600 mm, which had been packed in advance with a fixed layer (packing height 950 mm) of a treating agent consisting of 125 kg of 10 – 40 mesh active carbon on which had been deposited by adsorption thereto 22 kg of 2-mercaptobenzothiazole, the mercury concentration 25 hours later was 2 ppb and 170 hours later was 3 ppb.

Now, when the adsorbed mercury was desorbed and recovered and the anion exchange resin was regenerated but the fixed layer of the treating agent was left intact and the treatment of waste water containing 8200 ppb of mercury was carried out under substantially identical conditions as hereinabove, the mercury concentration in the waste water after 25 hours of treatment with the anion exchange resin was 340 ppb. When this waste water was further treated with the fixed layer of the treating agent, the mercury concentration was 3 ppb. On the other hand, the mercury concentration after 170 hours was 900 ppb after treatment with the anion exchange resin and 5 ppb after treatment with the treating agent. Further, when waste water containing 8000 – 10,000 ppb of mercury was treated under identical conditions while repeatedly carrying out the desorption and recovery of mercury of the anion exchange resin and its regeneration step, the number of days duration that the treating agent could stand use, i.e. the number of days until the mercury concentration in the waste water subsequent to the treatment with the fixed layer of the treating agent reaches 10 ppb, was 200 days.

EXAMPLES 70 – 73

Experiments were carried out as in Example 68, varying the carrier, the organic compound deposited thereon and the material treated. The results obtained are shown in Table 6.

TABLE 6

Experiment No.	Pretreatment Amount used of anionic exchange resin (g.)	Solid treating agent: Organic compound used: Name	Amount deposited (wt. percent)	Solvent used	Carrier: Name	Weight (g.)
Example 70	63	Thionalide	1.6	Acetone	Silica gel	120
Example 71	1,700	Pipecoline pipecolyl dithiocarbamate	5.0	3% aq. NaOH sol	Active carbon	1,000
Example 72	4,000	2-mercapyobenzothiazole	5.0	Same as above	do	1,600
Example 73	63	p-Dimethylaminobenzylidene rhodanine	4.0	Acetone	do	40

Experiment No.	Contact time with material treated or space velocity: Resin column (l./hr.)	Treating agent column (l./hr.)	Material treated: Metal to be removed	Property	Metal concentration (p.p.b.): Before treatment	After passage through resin column or after contact with resin	After passage through treating agent column (120 hrs. later) or after contact with treating agent
Example 70	3.0	1.9	Hg	Aq. waste water	7,000	240	5
Example 71	Contact time about 3 hours	Contact time about 2.5 hours.	Hg	do	11,600	900	4
Example 72	Contact time about 4 hours	Contact time about 2 hours	Hg	Aq. slurry	5,200	500	7
Example 73	2.0	2.0	Hg	Aq. sol	10,200	350	4

EXAMPLES 74 – 78 AND CONTROL 5

Fifty grams of thionalide in solution in 150 ml of dichloromethane were flowed down through a glass column of 8 mm inside diameter packed with 15 grams of a carrier material to cause the adsorption to and deposition on the carrier of the thionalide, followed by air drying and waterwashing the carrier. A solution containing 5600 ppb of mercury and 1500 ppb of copper was flowed down through the foregoing packed column, after which the metal concentration was measured with the results shown in Table 7. As can be seen from the results given in this table, better results are had by the use of carbon, silica gel and zeolite, as compared with the other readily available carrier materials such as alumina and magnesia.

TABLE 7

Experiment No.	Carrier	Organic compound	Metal concentration (p.p.b.) Before treatment Hg	Before treatment Cu	After treatment Hg	After treatment Cu
Example 74	Active carbon	Thionalide	5,600	1,500	50	10
Example 75	Silica gel	do	5,600	1,500	65	15
Example 76	Zeolite	do	5,600	1,500	60	15
Example 77	Alumina	do	5,600	1,500	590	550
Example 78	Magnesia	do	5,600	1,500	1,200	520
Control 5	Active carbon	None	5,600	1,500	2,100	1,000

We claim:

1. A treatment process for removing metals which comprises contacting a gaseous phase metal-containing material from which the metal is to be removed, with a solid treating agent consisting of a carrier material and a compound deposited thereon by absorption, said compound being selected from the group consisting of

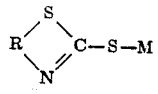
a. an organic compound capable of forming a mercaptide compound of a metal selected from:

1. mercaptide compounds of the formula

$$R—S—M$$

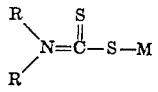
wherein R is an aromatic group or a group having a terminal —CH= or —CH_2— radical, and M is hydrogen or an alkali metal;

2. thiazole compounds of the formula



wherein R is an aromatic group and M is hydrogen or an alkali metal;

3. di-alkyldithiocarbamic acids of the formula



wherein R is a $C_1 - C_{10}$ alkyl radical and M is hydrogen or an alkali metal; and

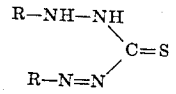
4. xanthates of the formula

$$R—O—C—S—M$$

wherein R is butyl or isopropyl and M is hydrogen or an alkali metal;

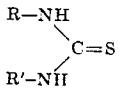
b. an organic compound capable of forming a mercaptide compound of a metal selected from:

1. thiocarbazones of the formula



wherein R is an aromatic group;

2. thioureas of the formula



wherein R and R′ are each an aromatic group or a $C_1 - C_{10}$ alkyl radical;

3. 2-Mercaptobenzimidazole; and

4. 1-Mercaptoimidazoline; and

(c) an organic compound capable of forming a chelate compound of a metal selected from anthranylic acid, oxine and 2-methyl oxine.

2. The process according to claim 1 wherein said carrier material is selected from the group consisting of carbon, silica gel, silica-alumina gel containing at least 50 percent by weight of silica gel, and zeolite.

3. The process of claim 1 wherein said metal-containing material from which the metal is to be removed by treatment is one containing a metal or metals selected from the group consisting of Hg, Au, Bi, Cd, Co, Cr, Cu, Ni, Pb, Zn, Ag, Mn, Fe, Mo, Ti, Mg and Al.

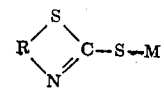
4. A treatment process for removing metals which comprises contacting a liquid phase metal-containing material from which the metal is to be removed, with a solid treating agent consisting of a carrier material and a compound deposited thereon by adsorption, said compound being selected from the group consisting of

a. an organic compound capable of forming a mercaptide compound of a metal selected from

1. mercaptide compounds of the formula

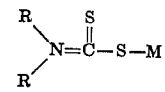
R—S—M wherein R is an aromatic group or a group having a terminal —CH= or —CH_2— radical, and M is hydrogen or an alkali metal;

2. thiazole compounds of the formula



wherein R is an aromatic group and M is hydrogen or an alkali metal;

3. di-alkyldithiocarbamic acids of the formula



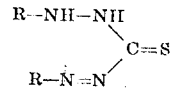
wherein R is a $C_1 - C_{10}$ alkyl radical and M is hydrogen or an alkali metal; and

4. xanthates of the formula

R—O—C—S—M wherein R is butyl or isopropyl and M is hydrogen or an alkali metal;

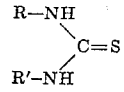
b. an organic compound capable of forming a mercaptide compound of a metal selected from

1. thiocarbazones of the formula



wherein R is an aromatic group;

2. thioureas of the formula



wherein R and R′ are each an aromatic group or a C_1 – C_{10} alkyl radical;

3. 2-Mercaptobenzimidazole; and

4. 2-Mercaptoimidazoline; and

c. an organic compound capable of forming a chelate compound of a metal selected from anthranylic acid, oxine and 2-methyl oxine.

5. The process of claim **4** wherein said metal-containing material from which the metal is to be removed by treatment has been pre-treated with an anion exchange resin.

6. The process according to claim **4** wherein said carrier material is selected from the group consisting of carbon, silica gel, silica-alumina gel containing at least 50 percent by weight of silica gel, and zeolite.

7. The process of claim **4** wherein said metal-containing material from which the metal is to be removed by treatment is one containing a metal or metals selected from the group consisting of Hg, Au, Bi, Cd, Co, Cr, Cu, Ni, Pb, Zn, Ag, Mn, Fe, Mo, Ti, Mg and Al.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,755,161 Dated August 28, 1973

Inventor(s) Noriyuki YOKOTA, Shingo TOKUDA, Yoshiro ITO and Hiroshi TAKATOMI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Claims, column 20, line 13: delete "4. 1-Mercaptoimidazoline; and" and insert --4. 2-Mercaptoimidazoline; and--

Signed and sealed this 25th day of December 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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